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ACCELERATING THE MARKETPLACE FOR RENEWABLE ENERGY TECHNOLOGIES

MICROWAVE HYDROGEN PRODUCTION FROM METHANE

Technical Report #: 1604-112

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Abbreviations and Acronyms

CARB	California Air Resources Board
CBD	Chemical Biological Defense
CEC	California Energy Commission
CH_4	methane
CO	Carbon Monoxide
DH_R	heat of reaction
EISG	Energy Innovation Small Grant
g/hr	grams per hour
GPM	gallon per minute
H_2	hydrogen
H_2O	steam, water
H_2S	hydrogen sulfide
hr	hour
kW	kilowatt
MW	Microwave
NOx	nitrogen oxides
O_2	oxygen
^oC	degrees Celsius
SBIR	Small Business Innovative Research
scfh	standard cubic feet per hour
SiC	silicon carbide
SMUD	Sacramento Municipal Utilities District
W	watt

1.0 Background

The Renewable Energy Testing Center (RETC) focuses on testing and validating renewable energy technologies related to biomass feedstock, with a particular focus on biofuels for transportation. The Renewable Energy Testing Center program also focuses on supporting relevant and emerging renewable energy technologies in the cellulosic waste, biomass-to-energy, and fuel conversion areas in support of the Department of Defense's (DOD) need for compliance with Executive Order 13423 which has set a goal for the DOD of increasing its alternative fuel consumption at least 10% annually. The RETC is using Technikon's world-class research, demonstration, and deployment facility located in the greater Sacramento, California region for these initiatives.

The development of renewable energy technologies presents a major opportunity for reducing U.S. dependence on foreign oil. The DOD, the Department of Energy (DOE), and private industry share the goal of reducing energy and fuel costs needed to support transportation, manufacturing, and the production of electricity. A major roadblock to the commercialization of renewable energy technologies is the need of smaller manufacturers to find a location to demonstrate and validate their pilot units. The RETC fills this need by supplying a third-party renewable energy testing and validation center, with a focus on systems meeting the renewable-fuel requirements of the DOD.

The RETC's objective is to provide private industry with an independent laboratory for the development of renewable energy and renewable fuels technologies and the evaluation of performance issues such as robustness, safety, energy efficiency, environmental effectiveness, and other key specifications. The RETC, and the oversight provided by RETC staff, brings together technology developers, government entities, and universities in a facility that provides the tools and services needed to bring renewable-energy systems to the commercialization phase. It also allows developers to integrate a variety of technologies into a complete waste-to-energy system at an accelerated pace and at a significant reduction in costs. Current state and federal grant structures are less flexible and almost exclude applications from smaller developers since they do not have the data they need to get an award. The RETC fills this funding gap, dramatically accelerating the commercialization of renewable energy technologies.

CHA Corporation has extensive experience developing microwave (MW) air, water and solids decontamination processes and completed 9 Small Business Innovated Research (SBIR) Phase I and 6 SBIR Phase II projects successfully. CHA is also ready for commercialization of previously developed MW technologies. CHA has fabricated and constructed many prototype MW systems for field demonstrations. Recently, CHA constructed two MW scrubbers and installed these microwave systems at Vandenberg Air Force Base. The Boeing Company is currently operating these units to destroy hypergolic fuel vapors and CHA is providing technical and operational assistance to Boeing. CHA constructed a prototype MW solids decontamination reactor system under a previous Army Chemical Biological Defense (CBD) Phase II SBIR (FY 2005-2009) and 2 gallon per minute (GPM) and 20-GPM mobile MW water treatment systems under the previous Army SBIR Phase II and Phase II Plus programs (FY 2003-2008).

In FY 2009 CHA completed the field demonstration of MW technology removing and destroying hydrogen sulfide (H_2S) and siloxanes from biogas produced by Sacramento Regional Wastewater Treatment Plant and Yolo Landfill site sponsored by Sacramento Municipal Utilities District (SMUD) and California Energy Commission (CEC). In FY 2010

CHA constructed a MW nitrogen oxides (NOx) removal unit for removing NOx and sulfur dioxide (SO_2) from the exhaust of 212 kilowatt (kW) engine running on biogas and is currently conducting the field demonstration of the unit at Tollenaar Dairy in Elk Grove, CA. SMUD, California Air Resources Board (CARB) and C-Micro Systems are providing financial assistance to CHA for this project.

CHA is currently working on an Energy Innovation Small Grant (EISG) project to produce hydrogen (H_2) from biogas for the pre-combustion NOx control for the biogas engine. The CEC sponsors this project.

Technikon and CHA Corporation are sharing the equipment, information and data from this activity between the EISG Grant and the RETC.

2.0 Microwave-Induced Steam-Methane Reforming

The steam (H_2O) -methane (CH_4) reforming process is used industrially to produce H_2 and carbon monoxide (CO). The following reactions represent the steam reforming of methane and other hydrocarbons, along with their respective heat of reaction (DH_R) [1].

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2 \qquad \Delta H_R > 0$$

Reaction 1

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H_R = +206\ kJ/mole$$

Reaction 2

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \Delta H_R = +165\ kJ/mole$$

Reaction 3

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_R = -41.2\ kJ/mole$$

Reaction 4

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H_R = -35.65\ kJ/mole$$

Reaction 5

Reaction 1 represents steam reforming of hydrocarbons in the mixture of hydrocarbons and water in vapor. Reaction 2 and Reaction 3 are applicable to the steam-methane reforming and Reaction 4 is applied to the water gas shift reactor. These reactions are achieved by passing the steam/feedstock mixture through the reformer tubes filled with a (usually nickel-based) catalyst. Because steam-hydrocarbon reforming is highly endothermic, high product gas outlet temperatures in the range of 750-1,000 degrees Celsius (°C) are favored[2]. The high reforming temperature creates difficulties for small-scale reformers. The use of partial oxidation of hydrocarbons shown in Reaction 5 is used to increase the hydrocarbon conversion.

Microwave energy enhances chemical reactions by reducing the activation energy and requires much lower temperatures for steam-hydrocarbon reforming[2]. Results obtained from steam-methane reforming experiments show that more than 80% methane conversion was obtained by using MW energy in a bed containing a mixture of silicon carbide (SiC) and nickel catalyst using the mixture of methane, steam, and oxygen O_2. The bed temperature for this test was roughly 500 °C.

[1] *Adris, A.M. et al, "Production of Pure Hydrogen by the Fluidized Bed Membrane Reactor", Proc. 14th World Hydrogen Energy Conference, Cession C2.6, Montreal, Canada, June, 2002.*

[2] *Cha, C.Y., "Process for Efficient Microwave Hydrogen Production", US Patent No. 6,592,723 B2, Jul. 15, 2003 and US Patent No. 6,783,632 B2, Aug. 31, 2004*

The process increases the hydrogen product by shifting the H_2/CO products from Reaction 2 to H_2/CO_2 products according to Reaction 3 at temperatures in the range of 200-400 °C in the presence of an iron-chromium or copper alloys catalyst. As microwave energy reduces the activation energy, the shift reaction will occur at a much lower temperature than 200-400 °C.

3.0 Experimental Data

3.1 Steam-Methane Reforming Experiments with Water Injection

CHA is currently conducting the steam-methane reforming tests using the lab-scale MW reformer system shown in Figure 1. The lower reactor was packed with silicon carbide to evaporate water to produce steam. The upper reactor was packed with the mixture of nickel catalyst and SiC to perform the reforming reaction. Each MW reactor is equipped with two 1-kW magnetrons.

Water was injected into the area between the upper and lower MW reactors. The mixture of CH_4 and O_2 entered into the bottom of the lower reactor. Figure 2 shows the CH_4 conversion efficiency as a function of the ratio of water injected to CH_4. The effects of methane, and water flow rates on the conversion efficiency have been investigated for CH_4 to O_2 ratio of 2. The CH_4 conversion efficiency increased when the ratio of water vapor to methane flow increased. The methane conversion efficiency target of 75% was achieved when the water vapor to methane ratio above 4. When this ratio was greater than 5, the CH_4 conversion efficiency increased to greater than 80% as shown in Figure 2.

A long-term test was conducted using 5 standard cubic feet per hour (scfh) CH_4, 2.5-scfh O_2, and about 28-scfh water vapor flow rate (630 grams per hour (g/hr)) for 200 minutes. The CH_4 conversion efficiency was greater than 80% and was very stable as shown in Figure 3.

Figure 1: Lab-Scale Microwave Reformer

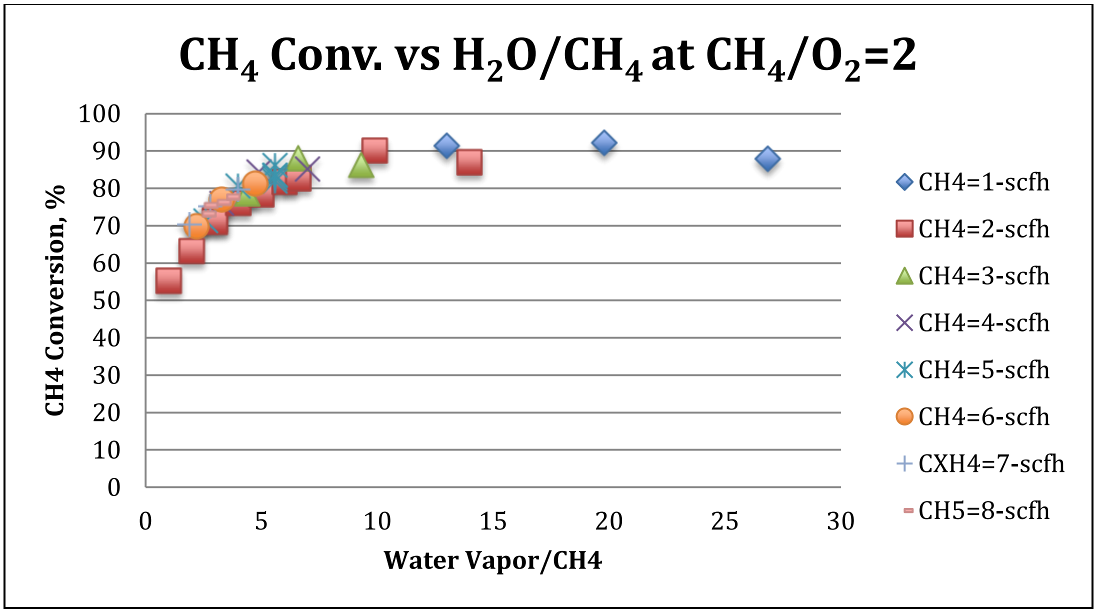

Figure 2: CH4 Conversion Efficiency as a Function of Volume Ratio of H2O to CH4

Because steam generation is energy intenisve, MW energy would typically not be used for steam generation as was done in the first series of tests. However, the data presented in Figure 2 and Figure 3 is valuable to determine the feasibility of the process and to work out any problems that might be encountered with the reforming method. The next serise of tests utilized a thermal steam generator.

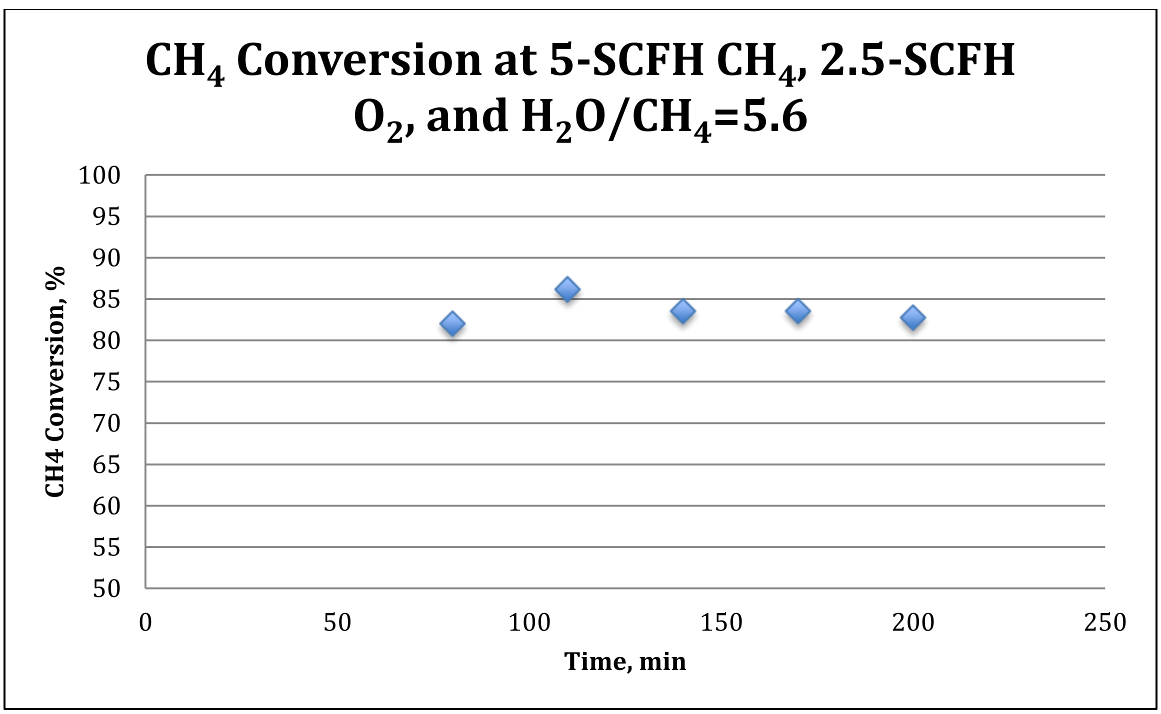

Figure 3: CH4 Conversion Efficiency at Various Test Times with Water

After the steam generator was installed, we completed a series of steam-methane reforming experiments with CH_4 flow rates in the range of 5- to 10-scfh. The CH_4 conversion efficiency increased as the ratio of steam to methane flow increased as shown in Figure 4.The CH_4 conversion efficiency was greater than 80% when the ratio of steam to CH_4 was in the range of 2 to 4 compared to a ratio between 5 and 20 when water injection was used in the first series of experiments. The main advantage of using steam instead of water injection into the lower SiC MW reactor was higher CH_4 conversion with much lower H_2O flow rate. It is also more favorable for higher CH_4 flow rates, increasing throughput over direct water injection.

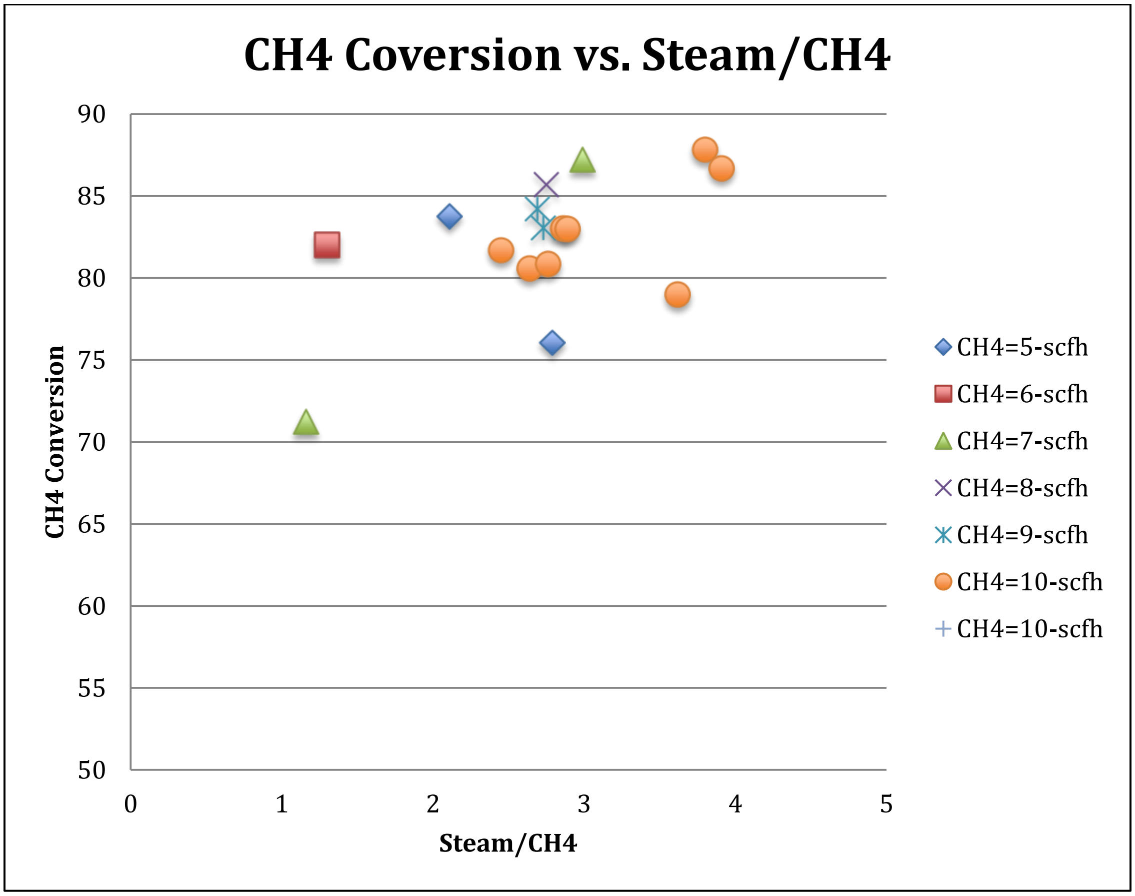

Figure 4: Steam Methane Reforming Test Results

A steam-methane reforming test was conducted for 360 minutes with 10-scfh CH_4, 5-scfh O_2 with the steam flow rate in the range of 564 to 825-g/hr. The steam flow rate fluctuated during this 6-hour (hr) test. However, the CH_4 conversion was stable at about 80% as shown in Figure 5. Table 1 presents the composition of the product gas from the microwave reformer. It is evident from these results that H_2 production can be increased by converting the CO in a water gas shift reactor.

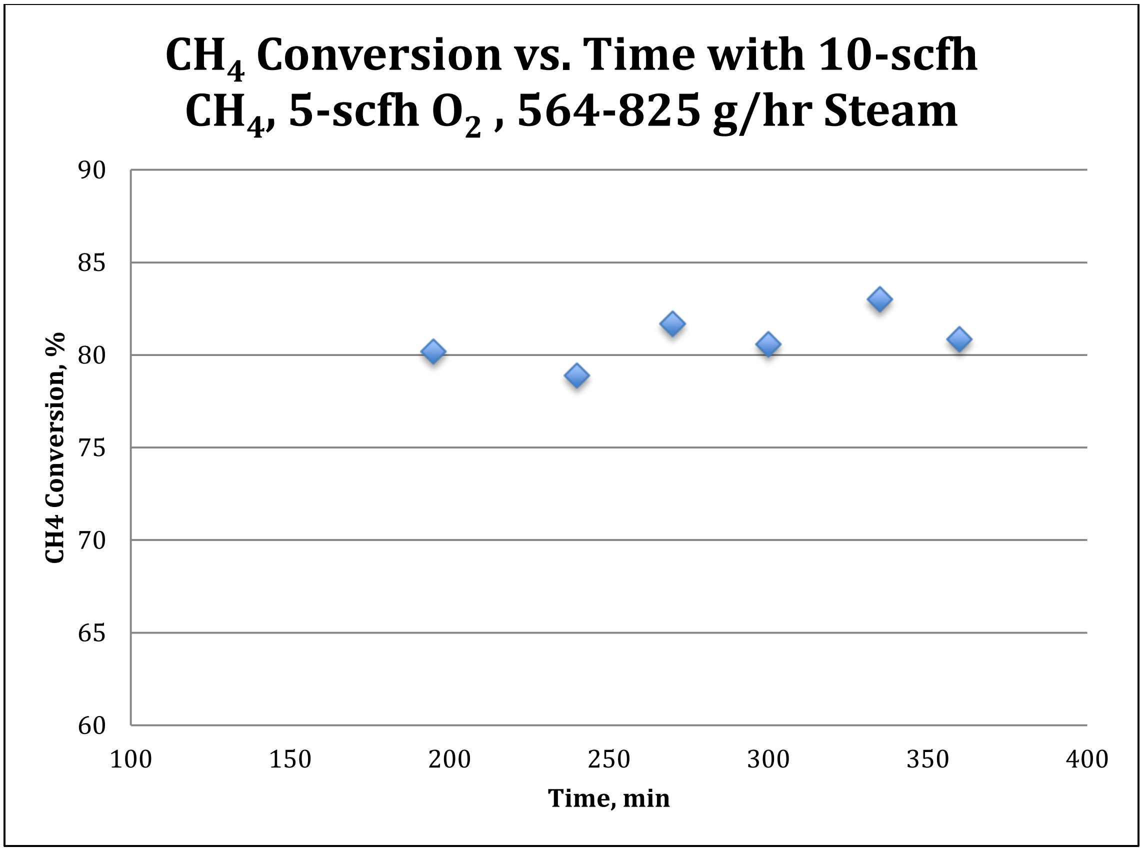

Figure 5: 6-hr Reforming Test with 10-scfh CH4, 5-scfh O2 with Steam

Table 1: Product Gas Composition (10-scfh CH4, 5-scfh O2, and 864 g/hr steam)

Gas Component	Volume %
Hydrogen	66.13
Methane	4.12
Carbon monoxide	14.20
Carbon dioxide	15.55

3.2 Scaled up Steam-Methane Reforming Experiments

A larger MW reactor was constructed using a 6-kW variable power Cober MW generator to investigate the effect of MW power on the CH4 conversion efficiency. Also, this reactor had a 3 inch quartz tube that was larger than the 2.36 inch tube used in the system from Figure 1. Figure 6 shows a picture of this MW reactor.

Figure 6: 6-kW Microwave Reactor System

The steam reforming tests were conducted in the 6-kW variable power microwave reactor. The CH_4 conversion efficiency increased as the MW power increased as shown in Figure 7. The CH4 conversion increased from 67 to 80% as the microwave power increased from 2.2 to 4.7-kW at a CH_4 flow rate of 17-scfh. Figure 8 shows the CH4 conversion efficiency as a function of CH4 flow rate at 4.7-kW MW power. The CH_4 conversion increased from 76 to 87% at 4.7-kW microwave power as the CH_4 flow rate decreased from 20 to 11-scfh.

When the CH_4 flow rate increased twice, the MW power requirement to obtain equivalent CH_4 conversion also doubled. The best ratios for the steam to CH_4 and O_2 to CH_4 are respectively 3 - 4 and 0.5 for hydrogen production using nickel catalyst. These higher flow rate tests indicate that the steam reforming process can be scale-up by using the ratio of 0.235 kW microwave power per scfh of CH_4 flow rate. As an example, the required microwave power for processing 30-scfh CH_4 flow rate will be 7-kW. The future challenges for the MW steam reforming are how to reduce the power requirement and reactor scale-up that overcomes the limitation of MW penetration depth.

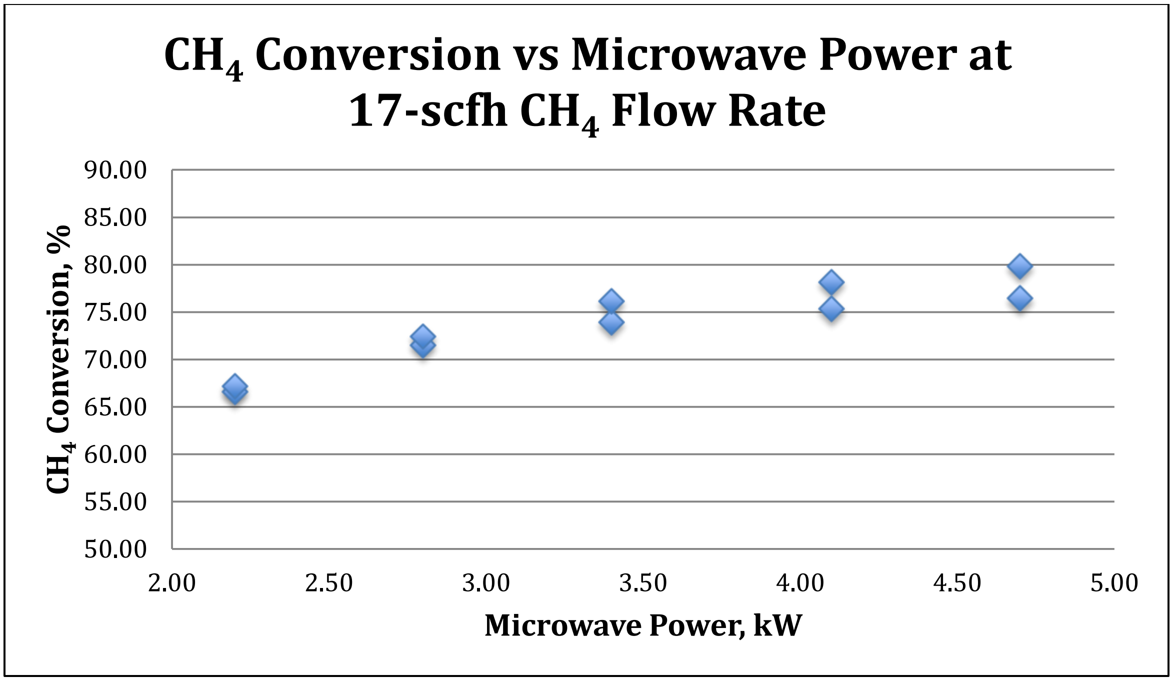

Figure 7: CH4 Conversion Efficiency as a Function of MW Power at 17-scfh CH4, 8.5-scfh O2 and 17-- g/hr steam

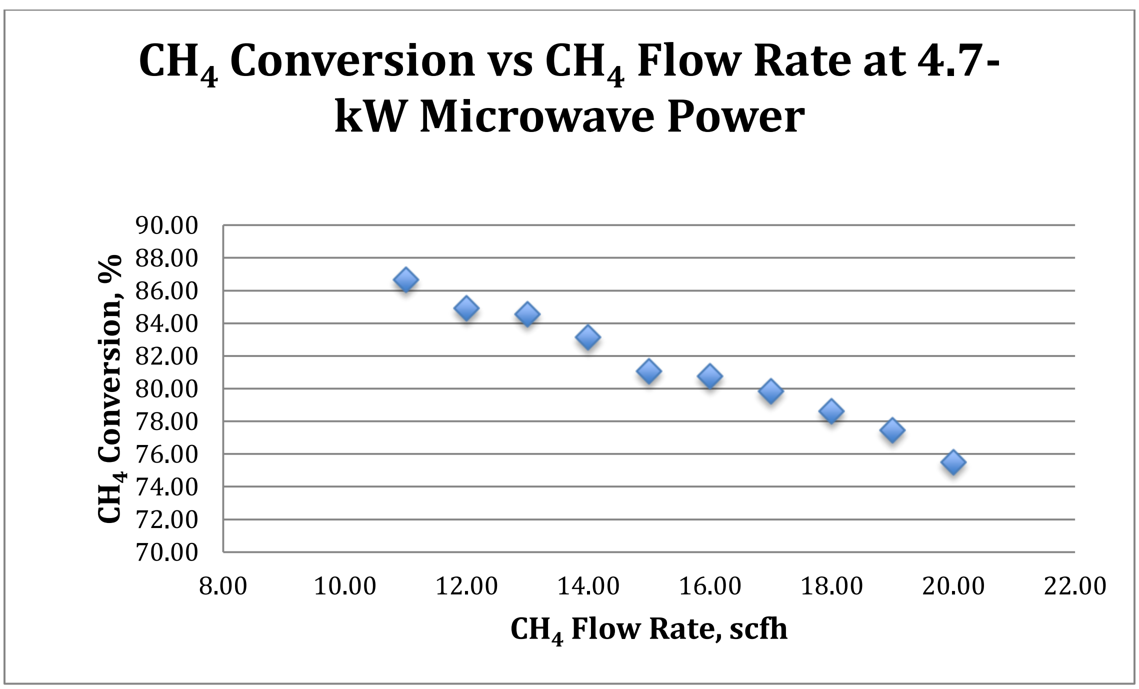

Figure 8: CH4 Conversion Efficiency as a Function of CH4 flow rate at CH4/O2=2 and steam/CH4=4.4

Table 2 presents typical test results obtained from the 6-kW MW reactor tests. From data shown in this table we estimated that about 60% of CO produced from CH_4 and O_2 was reacted with steam to produce H_2 and CO_2. When CO is converted into H_2, one mole of CH_4 produced 2.8 moles of H_2.

Table 2: Typical Results from 6-kW MW Reforming Tests

Process Conditions	
CH_4 Flow Rate	17-scfh
O_2 Flow Rate	8.5-scfh
Steam Flow Rate	1,700-g/hr
Product Gas	50.1-scfh
H_2 Production	33.1-scfh
CO Production	5.3-scfh
CO_2 Production	8.2-scfh
CH_4 Conversion	80%
CO Conversion	61%
Product Gas Composition	
Hydrogen	66.1%
Carbon Monoxide	10.7%
Carbon Dioxide	16.4%
Methane	6.8%
Total	100.0%

3.3 Microwave Water Gas Shift Reaction

We completed a series of tests for the water gas shift reaction using the 6-kW MW reactor shown in Figure 6. Table 3 and Figure 9 present test results for water gas shift investigation. Tests results indicate that the conversion of CO increased as the ratio of steam to CO flow rate increased and reached the maximum at the ratio of 2 and started to decrease with further increases to the steam to CO ratio. The microwave power required was only 600 watts (W), less than one-seventh of power used for the steam reforming reaction. Higher CO flow rate was more favorable to the CO conversion efficiency. The highest CO conversion efficiency was 98% at a flow rate of 21-scfh with the steam to CO ratio of about 2. We did not test with CO flow rates greater than 21-scfh but trend in Figure 9 indicate higher flow rates could be used in this reactor. Consequently, the use of microwave water gas shift reactor has greater prospects, especially converting CO in syngas produced from gasifiers to obtain an ideal H_2 to CO ratio of 2.

Table 3: Product Gas Composition from Water Gas Shift Reactor (21-scfh CO and 1,024-g/hr Steam at 600-W MW Power)

Gas Component	Volume %
Hydrogen	49.67
Carbon Monoxide	0.29
Carbon Dioxide	49.85
Hydrocarbons	0.18

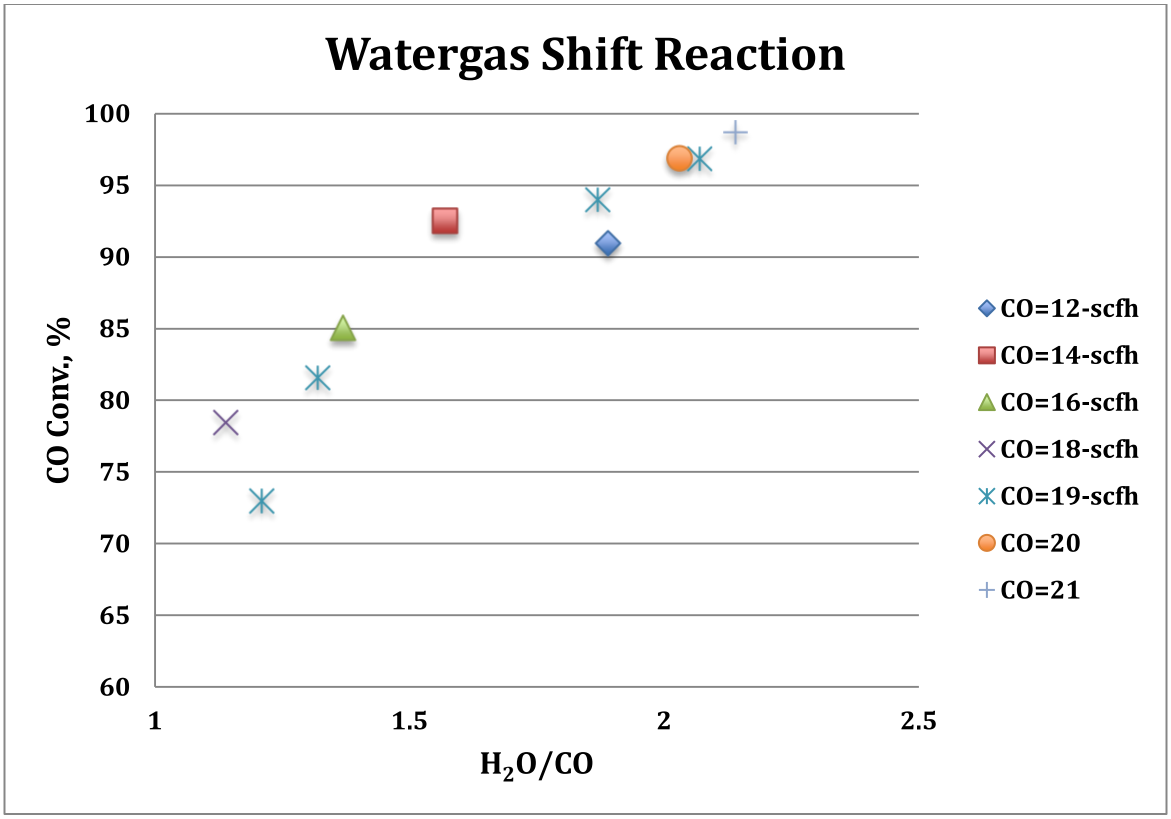

Figure 9: CO Conversion Efficiency as a Function of Steam to CO ratio at 600-W MW Power

4.0 Summary and Conclusion

The goal of this project is to determine the feasibility of using microwave-based production of hydrogen from hydrocarbons or biogas for pre-combustion NOx control of reciprocating engine exhaust and fuel cell application of biogas. Our target is to obtain the methane conversion efficiency greater than 75% in the presence of hydrogen sulfide.

We have completed a series of methane-steam reforming tests using the nickel catalyst by injecting water into the 2.36-inch microwave reactor to generate steam. The highest CH_4 conversion was 92% at 1.0-scfh methane, 0.5-scfh oxygen, and 450-g/hr water flow rates. The water vapor to CH_4 flow rate was a major controlling factor for the CH_4 conversion. The CH_4 conversions greater than 75% were obtained with water flow rate of 650 g/hr when the ratio of CH_4 to O_2 was 2 and the CH_4 flow rate was less than 8-scfh.

In addition, we completed a series of tests using a thermal steam generator in lieu of the water injection system for the CH_4 flow rate in the range of 5- to 10-scfh. Whenwater injection was replaced with steam generator, the ratio of steam to CH_4 that provides 80% conversion was much lower and our target on CH_4 conversion was achieved. A 6-hr test was conducted that show very stable CH_4 conversion around 80%. The best ratios of steam and O_2 to CH_4 flow rate were 3-4 and 0.5, respectively.

A new 6-kW microwave reactor was constructed using 3-inch quartz tube and used for completing a series of the microwave reforming tests using the CH_4 flow rates twice

greater than flow rate used in earlier tests. The microwave power required was 0.235-kW per scfh CH_4 flow rate, which agreed with results obtained from the 2-kW 2.6-inch reforming reactor. This factor may be used for the scale-up of microwave reforming process. The biggest challenge of microwave reforming process is how to reduce this power requirement for the pre-combustion NOx control and fuel cell applications.

The water gas shift reaction was studied using CO and steam. The microwave energy enhanced the water gas shift reaction significantly and required microwave power was only 600-W. The 98% of CO was converted into H_2 and CO_2 with 21-scfh CO flow rate with steam to CO ratio of 2 at 600-W. This microwave water gas shift reactor can be used to convert CO in gasifier syngas into H_2 to provide syngas with an ideal H_2 to CO ratio of 2 for Fischer-Tropsch conversion process.

The results of this testing program have been very promising, demonstrating the ability to achieve higher methane conversion than conventional methane steam reforming processes. In addition to the higher conversion efficiencies, the microwave reactor system used for the process is more easily scaled to lower gas production volumes than conventional reforming technologies. This makes the technology well suited to generate hydrogen from natural gas for hydrogen fuel cells in the 1 to 20-kW range. The next step in the process is to perform an economic comparison to current small scale hydrogen supply methods. This will be based on supplying hydrogen for a 5-kW fuel cell system. The capital and operating costs of the technology will be estimated and compared to compressed hydrogen delivery and onsite electrolysis.